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5**Energy Conversion and Management 88 (2014)** 1159–1166 **Contents lists available at ScienceDirect Energy Conversion and Management journal homepage: www.elsevier.com/locate/enconman** Transesterification **of**

3**soybean oil with methanol and acetic acid at lower reaction severity under subcritical conditions**

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13**of San Carlos – Talamban Campus, Nasipit, Talamban, Cebu City** 6000, **Philippines**

article info Article history: Available online 24 March 2014 Keywords: Biodiesel Soybean oil Subcritical methanol Subcritical acetic acid (trans)Esterification abstract Soybean oil (56–80 g) was reacted with methanol (40–106 mL) to produce fatty acid methyl ester in the presence of 1–6% acetic acid under subcritical condition at 250 °C. Stirring and loading of the reaction sys- tem affected the yield and severity of the process. The presence of acetic acid improved the yield of FAME from 32.1% to 89.5% at

11**a methanol to oil** molar **ratio of** 20 mL/g. **Acetic acid** was found **to**

act strongly as an acid catalyst and to some extent improved the solubility between oil and methanol. Reaction pressure higher than the supercritical pressure of methanol (7.85 MPa) was not required to achieve high FAME yield (89.5–94.8%) in short time (30–60 min).

 1. Introduction

After Saka and Kusdiana [1] introduced supercritical methanol technology to produce biodiesel in 2001, many authors have since then studied biodiesel production by utilizing the unique proper- ties exhibited by methanol under sub and supercritical conditions. Its main advantages include the fact that it requires a relatively shorter time (4–30 min) to produce high purity (>95%) fatty acid methyl esters (FAME) and its tolerance to impurities like water and free fatty acids (FFA), without the use of any catalysts [1–6]. Despite its many advantages over conventional acid and base catalyzed reactions, it has been greatly criticized for the high tem- perature (>300 °C) and high pressure (>20 MPa) required. Operat- ing at severe temperature and pressure conditions require a well engineered process that can efficiently recover the spent energy [7], which would need high capital cost and for the moment not fea- sible to commercialize. Another concern is

thermal degradation of the product at elevated temperatures. Imahara et al. [8] suggested that the supercritical methanol method should be carried out at temperature below 300 °C, preferably at 270 °C, with a pressure higher than 8.09 MPa. Shin et al. [9] reported that degradation of Abbreviations: FA, fatty acid; FAME, fatty acid methyl ester; FFA, free fatty acid; TC, critical temperature; PC, critical pressure; SOR, solvent to oil ratio. ⇑ Corresponding author. Tel.: +886 2 27376612. E-mail addresses: suryadiismadji@yahoo.com (S. Ismadji), yhju@mail.ntust. edu.tw (Y.-H. Ju).

presence of water, was observed at temperatures above 250

severity of the process, a two-step ap- proach was introduced by Kusdiana and Saka [10] in which hydro- lysis was followed by esterification. Fatty acids (FA) and glycerol were firstly produced during hydrolysis at 270 °C for 1 h. After that FAs were separated from glycerol and then esterified with metha- nol at 270 °C for 40 min to achieve an FAME yield of 94% [11]. This approach seems to use less severe operating conditions but re- quired a long reaction time, resulting in a lower overall productiv- ity and is less energy efficient due to cooling and heating in between steps. Later Minami and Saka [11] introduced an impor- tant concept of the catalytic activity of FAs during hydrolysis and esterification. This idea was accepted by some researchers and ap- plied it in the hydrolysis of sunflower oil [12] and Jatropha oil [13]. Chen et al. [13] added acetic acid in hydrolysis reaction as a cata- lyst instead of the common FAs found in vegetable oils. Some researchers disagree with this idea since there is certain limitation for FFA to act as an acid catalyst due to its lower extent of ioniza- tion and its large steric hindrance to form an active intermediate with triglyceride [14]. The use of supercritical methanol with ace- tic acid addition has been investigated by Wei et al. [15] in which high amount of methanol (up to 60 mol per mole of oil) and long reaction time (90 min) were required even

acetic acid as both a catalyst and a co-solvent has not been explored. This study aimed to investigate the production of FAME from soybean oil at 250 °C and attempted to utilize acetic acid as a cat- alyst and a co-solvent to reduce the amount of methanol required. The effects of reactor loading, pressure and stirring on FAME yield were also studied.

supermarket. Standards of FA, acylglycerides such as monoolein, diolein and triolein and FAMEs were obtained from Supelco (Belle- fonte, PA). All solvents and reagents used were either high perfor- mance liquid chromatography (HPLC) or analytical reagent grade, obtained from commercial sources. 2.2.

Transesterification reactions Soybean oil (56.6–80.0 g), acetic acid (0.1–40.0 mL) and metha- nol (40.0–106 mL) were weighed and added into a glass chamber (190 mL) and placed in a high-pressure reactor (290 mL). Unless otherwise specified, the reactions were carried out with a fix total volume of 170 mL, which is about 87% of the glass chamber capacity. A detailed reactor description is given elsewhere [16]. The reactor is equipped with an external electric heater and a mag- netic stirrer. Temperature in the reactor was controlled to within ±2 °C. After the sample was put in the reaction chamber, the reac- tor was sealed and the chamber was purged with N2. The reaction was carried out with constant stirring (300 rpm) at 250 °C to avoid thermal degradation for a predetermined time. Heating rate of the reactor was kept at 5 °C/min with a heating time of 40–45 min. The moment the reactor reached the desired temperature was counted as time zero. After the reaction, the reac- tor was rapidly cooled, pressure inside the reactor was released and product in the reactor was collected at room temperature. Methanol and acetic acid in the product were removed and recovered using a rotary evaporator (BUCHI Labortechnik AG in Flawil, Switzerland) operated at 40 °C and 13.3 kPa. The residual acetic acid and water were further removed by heating the mixture to 80 °C at 13.3 kPa. The collected product containing FAME was washed three times, each using 20 mL 5% NaCl solution, in a sepa- ration funnel to remove glycerol and residual acetic acid. The solu- tion was allowed to clarify in between washings. The upper FAME rich phase was withdrawn and dried using a rotary evaporator. The recovered product was weighed and analyzed for its FAME, FA and acylglyceride contents. Results of the reaction were evaluated in terms of FAME yield, conversion and productivity. FAME yield is defined as the mass of FAME (MFAME) produced per mass of oil (MOil) used in the reaction. This was calculated using Eq. (1), where AFAME is the area calculated from the GC anal- ysis and fc is the external calibration factor (slope of the calibration curve) while Cs and Vs are the concentrations and volumes of the samples prepared and injected to the GC for analysis, respectively. FAME yield ð%Þ ¼ MMFAOMilE 100% ¼ M product RAFAME f c MOil CsVs 100% ð1Þ Conversion of FAME was calculated using Eq. (2). The theoreti- cal FAME yield based on stoichiometry where 1 mol of triacylglyce- ride produces 3 mol of FAME was used as reference to incorporate the un-reacted partial glycerides and FFAs. Conversion ð%Þ ¼ FAME yield 100% ð2Þ Theoretical FAME yield Productivity is an important parameter in chemical processes but is often overlooked. Eq. (3) was utilized to calculate the pro- ductivity, which is defined as the amount of FAME (MFAME) pro- duced per reactor volume (Vr = 240 mL) per reaction time (t). kg Productivity L h ¼ MFAME Vrt ð3Þ Experiments were carried out in triplicates and values reported are average values of the triplicate trials. 2.3. Gas chromatography analysis A 20 mg aliquot of the lipid sample was dissolved in ethyl ace- tate and filtered through a 0.2 lm PTFE hydrophobic membrane to remove moisture. From this prepared solution, a 1.0 lL sample was injected into a high temperature gas chromatography (HTGC) for analysis. External calibration curve was generated using 0.2– 20 mg of a pure standard dissolved in ethyl acetate. The calibration curve was generated by fitting a straight line with the y-intercept passing through zero ($R^2 > 0.99$). Qualitative and quantitative analyses of FAME and un-reacted FFA in each sample were performed using a Shimadzu GC2010 (Kyoto, Japan) equipped with a split-injector and a FID. Separation was

4**carried out on a ZB-5HT (5% phenyl)-methylpolysiloxane non- polar column (15 m 0.32 mm i.d., 0.1 mm film thickness)**

(Zeb- ron, Phenomenex, Torrance, CA, USA). Both injector and detector temperatures were set at 370 °C. The column temperature was programmed to increase at a rate of 15.0 °C/min from 80 °C to 365 °C and held at 365 °C for 48 s. N2 was used as the carrier gas with a linear velocity of 30 cm/s at 80 °C. Data analyses were car- ried out by the software ‘‘GC Solution version 2.3’’, Shimadzu. 3. Results and discussion 3.1. Effects of reactor loading and pressure In principle the effect of pressure can only be accurately inves-

tigated using a tubular flow reactor where pressure can be con- trolled via a backpressure regulator. For a batch reactor altering the initial amounts of oil and methanol could change the reactor pressure. However there have been various interpretations with regards to initial amount of reactants charged into a batch reactor. Some authors chose to carry out reactions with fixed amount of oil and varying the amount of methanol to investigate the effects of methanol to oil ratio and used an inert gas like nitrogen to main- tain a given final pressure [13,15]. Fig. 1 shows the effects of sol- vent to oil ratio at a fixed amount of soybean oil. Apparently the increase in solvent to oil ratio (SOR) resulted in an increase in FAME yield since forward reaction during transesterification was favored in the presence of excess methanol. Some researchers varied the amounts of reactant but used only a fixed percentage of the total reactor volume [17,18]. Fig. 2 shows the effects of the reactor loading at a fixed SOR on FAME yield and reactor pressure. It is evident that FAME yield and reactor pressure both increased with increasing reactor loading. A higher reactor loading corresponds to a smaller void volume, which serves as space for expansion of reactants. Since methanol has much lower boiling point (68 °C) than oil or any of the reaction products, it is safe to assume that part of methanol occupies the void space as va- por. If smaller space is available for the vapor at a fixed tempera- ture, it results in higher system pressure. It was also observed that reactor pressure decreased as reaction proceeded. In batch reaction, pressure changes in the course of reaction due to chang- ing amounts of reactants and products [19]. Nevertheless, it can be observed from the results that it is not necessary to reach the A.W. Go

2**et al. / Energy Conversion and Management** 88 **(2014)** 1159–1166 1161 **Fig. 1.** Effects **of**

solvent loading at a fixed amount of oil (5 g) and solvent composition (acetic acid:methanol = 1:3, v/v). Reactions were carried out at 250 °C for 60 min with constant stirring and pressurized to 10.0 MPa using N2. (a) (b) Fig. 2. Effects of reactor loading at a fixed solvent (acetic acid + methanol) to oil ratio of 1 mL/g. Reactions were carried out at 250 °C for 60 min with constant stirring and without any pressurizing gas. (a) FAME yield and (b) reactor pressure. supercritical pressure of methanol (8.1 MPa) in order for the reac- tion to take place and achieve high FAME yield. From a comparison of the results in Figs. 1 and 2, it can clearly be seen that with the same initial amount of oil (5 g), the same SOR and the same reactor loading (5%), the addition of an inert gas to pressurize the reactor did not improve the FAME yield. The addi- tion of inert gas as a third component to improve the solubility and pressure has previously been found to have no positive effects on FAME yield [6,20].

16**Imahara et al.** [20] suggested **that the** pres- ence **of** a **third component**

(N2 or CO2) tends to dilute the reaction system. This was also observed in this study, where FAME yield was found to be higher (56.9%) compared to that pressurized with N2 (48.6%). In addition a high FAME yield (80–90%) can be achieved at a lower SOR (1 mL/g) and at a higher reactor loading (87%). The importance of these results is that although pressurized reactor seems to provide logical results, which were usually ob- served (FAME yield increased with increasing SOR); it provides a misleading impression that high SOR and pressure are required to achieve high FAME yield. Minimizing void or maximizing the utilization of reactor volume is important to induce an increase in reactor pressure and reduce the amount of methanol in the va- por phase. Inert gas could be used to increase the reactor pressure but could not effectively drive the vaporized methanol back to the liquid phase. 3.2. Effects of stirring and addition of acetic

acid The effect of stirring was investigated is in supercritical metha- nol transesterification reaction in the presence of a co-solvent and conclusion was made that stirring has no positive effect on reac- tion [21], since the reactants are often claimed to be in a single supercritical phase. Moreover, most studies were carried out in small reactors made of stainless steel tube fittings and parts with size ranging from 5 to 10 mL, thus stirring was not possible [2,3,7,17]. Mixing in these small reactors may not be required due to the bigger surface area of contact between oil and methanol owing to its small diameter and longer reactor body, typically ori- ented horizontally. In their study, Glisic and Skala [22] observed that at temperatures below 240 °C, two to four distinct phases of the various product mixtures coexisted and predicted that single supercritical phase exists only at temperatures over 270

10**°C and** at **a methanol to oil molar ratio of**

42. Fig. 3 shows the effect of stirring on FAME yield. It can be seen that without stirring the doubling of SOR resulted in a twofold in- crease of FAME yield from 19.2% to 38.0%, consistent with most observations reported in literature that an increase in methanol amount resulted in improved in FAME yield [4,5,18]. Upon stirring higher FAME yields were obtained due to better contact between reactants. Although in this study observation could not be made at high temperature such as 250 °C, by applying stirring at room temperature a suspension of microsphere-like oil globules sus- Fig. 3. Effects of stirring and addition of acetic acid (6.25 wt.% based on oil) at a fixed reactor loading (87%) and methanol to oil ratio. Reactions were carried out at 250 °C for 60 min with a system pressure of 6.5–7.5 MPa. pended in methanol was observed. Thus stirring did increase the surface area of contact between oil and methanol during reaction at high temperature. The addition of acetic acid (6.25%) in metha- nol resulted in surprisingly high FAME yields of 89.5% and 93.4% at an SOR of 1 and 1.9 mL/g, respectively. Acetic acid could have aided the reaction by: Acting as an acid catalyst during the reaction.

3**Improving the inter-solubility between reactants by acting as a co-solvent.**

The possible formation of methyl acetate through the methyla- tion of acetic acid, which is known to act as a good solvent for lipids and is miscible with methanol. 3.3. Effects of SOR and amount of acetic acid in solvent As discussed in the previous section the FAME yield obtained at 250 °C was improved upon stirring, while increasing SOR, FAME yield can be increased to a greater extent. However the presence of acetic acid significantly lowered down the difference between FAME yields obtained at the two different SOR (1 and 1.9 mL/g) investigated. These results suggest that high FAME yield could be achieved at SOR lower than that used in supercritical methanol method (typically 1.9 mL/g or 42:1 M ratio of methanol to oil) [5]. The effects of SOR and amount of acetic acid on FAME yield and conversion were investigated and the results are shown in Table 1. Both optimum FAME yield and conversion of about 95% were ob- tained at

11**a methanol to oil ratio of** 35 **and** a **acetic acid of**

6.25 wt.% (based on oil). For reactions carried out without the addi- tion of acetic acid, FAME yield and conversion increased by 145% when the amount of methanol present in the system was doubled. Addition of acetic acid at the same amount of methanol to oil ratio resulted in significant increase in FAME yield and conversion. How- ever, by adding the same amount of acetic acid per gram of oil, the effect of increasing

methanol to oil ratio on the increase of FAME yield and conversion is insignificant (p = 0.05). In view of productivity, reactions carried out without acetic acid have productivities directly proportional to the methanol to oil ra- tio. Reactions carried out with the addition of acetic acid, on the other hand resulted in productivities which are inversely propor- tional to methanol to oil ratio. This is because experiments were carried out at a fixed volume (166–170 mL) and the amount of oil processed per batch decreased with increasing methanol to oil ratio. Since FAME yield for reactions with acetic acid are about 89– 95%, the amount of oil processed per batch becomes the main factor that affects the overall productivity of the process. Thus a methanol to oil ratio of 20 is preferable as this resulted in the high- est productivity (0.3 kg L 1 h 1). In Table 1, all reactions were carried out for 1 h. By increasing methanol to oil ratio, the same FAME yield can be achieved in a shorter reaction time as shown in Fig. 4. It can be seen that reaction carried out at higher methanol to oil ratio (35:1) resulted in high FAME yield (89.5%) in shorter time (30 min) compared to the same FAME obtained when using a lower methanol to oil ratio (20:1) that required a longer reaction time (1 h). The time required to ob- tain the same FAME yield was cut down by half, when the amount of methanol utilized was almost doubled, resulting in comparable productivities. Although higher amount of methanol utilized can be compensated by shorter reaction time, environmental concerns and overall economics of the process should be taken into account. A high initial methanol loading would result in large excess of methanol together with the product stream that needs to be recy- cled. A life cycle analysis on supercritical methanol process by Kiwjaroun et al. [23] showed that recycling of excess methanol consumes more energy than feedstock pumping and reactor heat- Fig. 4. Effects of reaction time on FAME yield at different methanol to oil ratios. Acetic acid (6.25 wt.% based on oil) was added. Reactions were carried out at a fixed reactor loading (87%), 250 °C for 60 min with constant stirring. Table 1 Effects of

17**methanol to oil ratio on FAME yield,**

conversion and productivity with varied amounts of acetic acid.

17**Reactions were carried out** with **constant stirring** (300 rpm) **at** 250 **°C**

for 1 h. Methanol:oil ratio Oil (g) Methanol (mL) AA (mL) Total volume (mL) FAME yield (%)* Total FAME (g) Conversion (%) Productivity (kg/L/h) No acetic acid added 21 80.0 80.0 42 56.5 109.0 3.125 wt.% acetic acid based on oil 20 80.0 77.5 25 73.0 89.5 30 67.0 95.9 35 61.0 102 40 56.5 108 6.25 wt.% acetic acid based on oil 20 80.0 25 73.0 30 67.0 35 61.0 40 56.5 – – 2.5 2.3 2.1 2.0 1.8 75.0 5.0 87.5 4.5 93.8 4.2 100 4.0 105 3.5 166 32.1a 168 78.8b 166 91.7c 170 93.6c 170 94.5c 169 94.4c 169 93.8c 166 89.5c 170 91.3c 170 94.8c 169 94.9c 169 93.4c 25.7 32.0 44.5 78.6 73.4 91.3 68.3 93.2 63.3 94.1 57.6 94.1 53.0 93.5 71.6 89.1 66.6 90.8 63.5 93.4 58.4 95.3 53.2 93.7 0.11 0.18 0.30 0.28 0.26 0.24 0.22 0.30 0.28 0.26 0.24 0.22 * Average value of 3 independent experiments with an uncertainty of ±1.7%,

12**means followed by the same letter do not differ significantly** from one another **(p = 0.05),** by **Duncan's** multi **-range test. A.**

W. Go et al. / Energy Conversion and Management 88 (2014) 1159–1166 1163 Table 2 Effects of acetic acid to methanol ratio on FAME yield. Reactions were carried out at a fixed solvent to oil ratio of 1 mL/g, a reactor

loading of 87% with constant stirring (300 rpm) at 250 °C for 1 h. 80 mL Solvent mixture (methanol + AA) % AA 0.0 80 g Oil Yield FAME 32.1 FFA 0.5 MG 9.1 DG 29.7 TG 27.0 0.1 0.6 45.2 85.8 0.5 0.5 11.9 4.0 23.8 4.4 17.9 5.1 1.3 3.1 91.6 91.6 0.6 0.6 4.0 4.6 0.3 0.6 2.3 0.3 6.3 12.5 89.5 84.7 0.8 0.5 5.7 11.1 1.7 3.5 2.2 1.0 18.8 25 83.6 77.3 2.3 2.7 9.5 12.9 3.5 6.9 0.8 0.7 37.5 50.0 69.0 62.8 13.8 17.0 12.0 11.9 4.5 6.7 0.6 0.6 Fig. 5. Reaction time courses. Reaction conditions: methanol to oil molar ratio = 20:1; 6.25 wt.% acetic acid (based on oil); reactor loading (87%); reaction temperature = 250 °C; reaction time = 60 min; with constant stirring. ing, which at the same time generating significant amount of envi- ronmental load. 3.4. Effects of acetic acid to methanol ratio Table 2 summarizes FAME yields obtained using different acetic acid to methanol ratios in the solvent (acetic acid + methanol). It seems that optimum FAME yield could be achieved by using 1– 6% acetic acid in the solvent. As the amount of acetic acid in- creased, the

14**amount of free fatty acid** (FFA) **in the** product also **in-** creased. Since **the**

total solvent amount was fixed (80 mL), methanol amount decreased with increasing acetic acid amount. Thus the FFA released was not effectively converted to FAME or probably at a slower rate. Beyond the optimum acetic acid amount, the amount of monoglycerides in the product also increased with increasing acetic acid concentrations, which may be due to the re- verse reaction as more FFA was released in the presence of lesser amount of methanol. This result suggests that the reaction proceeded firstly by the transesterification of acetic acid with tri- glycerides, which releases FFA. Saka et al. [24] reported that the transesterification of triglycer- ides with acetic acid has higher reactivity than that of the super- critical methylation using methanol or methyl acetate. The activation energy for the transesterification reaction between tri- glyceride and acetic acid was not specified, but an estimated value of 44.2 kJ mol 1 at 250–320 °C was obtained from their result [24]. This activation energy is lower than the activation energy of the supercritical methanolysis of triglycerides (69.2–92.0 kJ mol 1 at 200–300 °C) [1,6,24] and the activation energy of the esterifica- tion of oleic acid (54.7 kJ mol 1 and 176.9 kJ mol 1 at the subcriti- cal and supercritical state of methanol) [6]. This further supports the mechanism of that the reaction proceeds firstly with the transesterification of triglyceride with acetic acid, followed by the esterification of the FFAs released, which are more reactive than triglyceride; thus also explains the lower temperature re- quired for the reaction to proceed. Although acetic acid could be consumed as the reaction proceeds, an equimolar amount of FAs is generated, which is believed to have the same catalytic effect [24]. Taking into consideration that water is produced as a by- product during esterification, acetic acid could be regenerated as a product of hydrolysis reaction. Fig. 5 shows the time courses of the reaction. It can be seen that reactions are less likely to proceed at temperatures below 200 °C (during heating) and a steep increase in FAME yield was observed at 250 °C (45 min). The reaction approached equilibrium in 45 min at 250 °C. Extending reaction time up to 120 min did not result in higher FAME yield. At 200 °C even prolonging reaction time to 120 min only resulted in a FAME yield of 34% (data not shown). 3.5. Catalytic activity of acetic acid As mentioned previously, there is disagreement between the proposed catalytic effect of FFA as a week organic acid [11,23] and the limitation of FFA to catalyze (trans)esterification due to Fig. 6. Effects of FFA content on

10**FAME yield. Reaction conditions: methanol to oil molar ratio** = 20 **:1;**

6.25 wt.% acetic acid (based on oil); reactor loading (87%); reaction temperature = 250 °C; reaction time = 60 min; with constant stirring. Table 3 Comparison with other sub and supercritical methanol processes. Oil Methanol:oil ratio Stirring (rpm) Temp. (°C) Pressure (MPa) Time (h) FAME yield (%) Refs. Rapeseed

Soybean 5:1 methanol to CO2 Soybean 20:1 methanol to propane Soybean 42 42 24 – 300 – Pressurized with CO2 60 – Coconut 42 – Soybean 36 1000 Sunflower Pressurized with CO2 25 – Coconut 10:1 methanol to ether 30 – Rapeseed 36 400 Soybean 42 300 Soybean 1% K3PO4 24 – Soybean 0.5% Na2SiO3 36 – Soybean 4.0% H2SO4 and carbon dioxide 12 – Soybean 3.1% AA 30 300 Soybean 3.1% AA 30 300 Soybean 6.25% AA 20 300 350 45.0 300 20.0 280 12.8 280 20.0 350 19.0 250 24.0 320 10.0 305 – 250 10.2 350 – 220 – 220 3.0 70 10.0 250 7.2 (65)a 250 7.2 (62)a 250 7.0 (62)a 0.5 90.6 0.2 98 1.5 97.8 0.1 95 0.5 94 0.4 70 0.33 85 0.33 10 0.17 95 0.5 95.6 0.5 95.6 4.0 99 0.5 89.5 1.0 94.8 1.0 91.3 [1] [26] [4] [15] [5] [25] [6] [21] [27] [28] [29] [30] [31] This study This study This study a System pressure upon reaching 250 °C (at the end of the reaction). steric hindrance caused by its molecular structure and size [14]. Acetic acid is a better catalyst than FAs as it would be less sterically hindered from a structural and mechanistic point of view. From Fig. 6, it is clear that without the presence of acetic acid FAME yield increased with increasing initial FFA content in feed- stock oil. The addition of acetic acid (6.25 wt.% based on oil) re- sulted in the same FAME yield regardless of the initial FFA content in the oil. These results further suggest

9**that acetic acid** did **act as an acid catalyst**

and has a much stronger catalytic activ- ity than long chain FFAs. Prior to reaction it was observed that solubility of oil in metha- nol increased with increasing amount of initial FFA in the oil. At an initial FFA content of 50%, a homogeneous mixture of the reactants was formed even at room temperature. Thus the presence of FFA acted more as a co-solvent than a catalyst during the reaction. 3.6. Process evaluation Table 3 is a comparison of results of this study with those of some sub- and supercritical processes reported in literatures. Most processes required high methanol to oil ratio (>40), high tempera- ture (>300 °C) and high pressure (>20 MPa). Processes that were capable of lowering down the methanol ratio to 24 typically re- quired the use of a co-solvent, which in turn still resulted in a high- er overall solvent to oil ratio. Gaseous solvents like propane [4] have been successfully utilized to lower down both temperature and methanol loading but might involve greater risk during oper- ation. The use of carbon dioxide as a green co-solvent resulted in varying results. For some it was able to lower down the operating temperature but not the methanol to oil ratio [26], while others re- ported no positive effect on FAME yield and operating severity [6,20]. Although different feedstocks have been used, vigorous stir- ring at 1000 rpm [25] resulted in high FAME yield compared to that stirred at 400 rpm [27]. Other attempts to operate at subcritical methanol conditions in- clude the use of low concentration of insoluble base (K3PO4 and Na2SiO3) as heterogeneous catalyst in the reaction for ease of recovery. Reactions through this approach achieved high yields (96%) at relatively lower temperature (220 °C) and pressure (3.0 MPa) over

15**a short reaction time of** 30 **min** [29,30]. Compared **to the**

proposed method in this study, the use of K3PO4 was found to have its shortcomings if there is FFA. The presence of 1% FFA re- sulted in a decrease of yield from 96% to 87% and further to 51% when FFA was increased to 15% [29]. As solid catalyst recov- ery for both K3PO4 and Na2SiO3 seem to be easier but in the case of Na2SiO3 calcination at 400 °C for 4 h was required before reutiliz- ing the catalyst [30]. The use of acid like sulfuric acid was also em- Fig. 7. Pseudo-critical temperature and pressure of methanol–oil mixture esti- mated by Lorentz–Berthlot type mixing rules [5]. A.W. Go

2**et al. / Energy Conversion and Management** 88 **(2014)** 1159–1166 1165 **Table 4**

Predictions of pseudo-critical temperature and pressure of methanol–acetic acid mixture estimated by Lorentz–Berthlot type mixing rules [5]. Properties Units Methanol Acetic acid (%) Acetic acid 5 10 15 20 25 30 40 50 MW g/mol Tc °C Pc MPa Vc m3/kmol Zc 32.0 33.1 240 243 8.10 7.92 0.12 0.12 0.22 0.22 34.09 35.15 246 250 7.82 7.71 0.12 0.12 0.22 0.22 36.25 37.39 253 257 7.61 7.51 0.13 0.13 0.22 0.22 38.56 41.03 261 268 7.43 7.18 0.13 0.14 0.22 0.22 43.7 60.0 276 319 6.96 5.79 0.143 0.18 0.22 0.21 ployed together with CO2 as co-solvent to achieve complete con- version at low temperatures of 70–90 °C [31]. Again the problem of catalyst recycling or disposal becomes a major hindrance in an environmental point of view and the use of carbon dioxide at a high pressure of 10 MPa would still require pressurized vessels like any sub and supercritical transesterification processes. In a technoeconomic study by Marchetti and Errazu [32] the major cost indicators of a supercritical biodiesel plant are operat- ing cost and cost of raw material, which were found nearly twice of that required by other process. A separate study by Marchetti [33] on the economical variables in supercritical biodiesel showed that changes in methanol price could result in as much as 82% de- crease in the internal rate of return. These are mainly due to the se- vere operating conditions and high amounts of methanol required for the process. Moreover it was found that the high investment for supercritical methanol technology is required due to the high tem- perature and high-pressure reactor (350 °C and 20 MPa) [33]. The addition of acetic acid made it possible to obtain high FAME yield at lower severity (250 °C, 7.0 MPa) by using lower methanol to oil ratio (20–30 mol per mole oil) with moderate stirring. Acetic acid can easily be recovered together with methanol in the down stream process by evaporating or distilling during solvent recov- ery. It was observed in this study that in the recovery of solvents, the products was separated into a glycerol-rich bottom layer and a FAME-rich upper layer. Separation of glycerol and FAME is also relatively easy similar to that in the supercritical methanol processes. The use of the terminology ‘‘supercritical methanol process’’ of- ten leads to confusion as to whether the entire reaction system is at supercritical state or only methanol is at supercritical state. Methanol is at supercritical state as long as the temperature ex- ceeds 240 °C and pressure exceeds 8.1 MPa. However, the super- critical temperature (Tc) of oil is much higher than that of methanol. By using the

16**Constantinou and Gani (CG) method of group contributions**

[34], and the pseudo-triglyceride model pro- posed by Espinosa et al. [35] the Tc and critical pressure (Pc) of soy- bean oil can be estimated and is found to be 698.3 °C and 0.34 MPa, respectively. Fig. 7 shows that the pseudo Tc and Pc of methanol–oil mixture obtained by Lorentz–Berthlot type mixing rules [5]. It indicates that as methanol content increases, Tc decreases while Pc increases. Single phase could be achieved at 300 °C at an SOR of 1.9 mL/g, or

14**a methanol to oil molar ratio of 42.**

At lower methanol loading a sin- gle-phase pseudo-critical state could not be guaranteed. As shown in Table 4, the presence of acetic acid helps lowering the Pc but slightly increases the Tc of the methanol–acetic acid mix- ture. Thus in this study, the operating temperature (250 °C) ex- ceeded the Tc of the solvent mixture (243 °C) but the pressure (6.5–7.5 MPa) was lower than Pc of the solvent mixture (7.9 MPa). If the presence

of oil is taken into consideration, Tc of the oil– methanol–acetic acid mixture should be much higher (according to Fig. 7 >325 °C) thus the operation temperature used in this study (250 °C) is lower than the mixtures apparent Tc. Although the pres- ence of oil induces a decrease in Pc, the operation pressure (6.5–7.5 MPa) used in this study is lower than Pc of the mixture. Thus the oil–methanol–acetic acid mixture investigated in this study is believed to be in subcritical state. 4. Conclusion It was found in this study that pressure higher than Pc of meth- anol is not necessarily required to achieve high FAME yield. Stirring improved FAME yield which helps justifying that the reactions were carried out under subcritical condition. The use of acetic acid to improve FAME yield under subcritical condition was also inves- tigated in this study. The addition of acetic acid was able to lower down the reaction temperature from higher than 300 °C, which is typically required in supercritical methanol processes, to 250 °C and still achieving high yield (90–95%) in reasonable short time (30–60 min). Acetic acid was found to act strongly as an acid cata- lyst and improve the solubility between oil and methanol. An opti- mization of the process may lead to reduction of the required methanol to as much as 20 mol per mole of oil without signifi- cantly affecting the FAME yield.

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